

PATENT SPECIFICATION



DRAWINGS ATTACHED

896,866

Inventor: ERNEST RUSSEL BOLLER

Date of Application and filing Complete Specification: May 27, 1960.

No. 18897/60.

Complete Specification Published: May 23, 1962.

Index at Acceptance:—Class 82(2), F1(A:B3), F2(A:B:D:F:G:M:Q:R:U:Z2), F4(E:F:K:W), G1, G2(A:B:D:F:G:M:Q:R:U:Z2), G6, G14(E:F:K:W).

International Classification:—C23c.

COMPLETE SPECIFICATION

Process for Coating Ferrous Metals

We, THE BOLLER DEVELOPMENT CORPORATION, a corporation duly organized and existing under the laws of the State of Indiana, United States of America, of 410 Glass Block, Marion, State of Indiana, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns a process for applying a protective coating to ferrous articles which comprises first plating the ferrous surface with a non-ferrous metal having a low solubility in liquid aluminum and then applying a hot-dipped aluminum or aluminum alloy coating. The first coating may be chemically plated, i.e., galvanically deposited; or it may be electroplated. In either case the plating is applied from an anhydrous metal chloride bath at an elevated temperature. The metal applied for this primary coating should have a solubility in liquid aluminum not exceeding 8% by weight at 700°C. Such metals are chromium, nickel, lead, titanium, molybdenum, beryllium, bismuth, cobalt, manganese, antimony, tungsten and zirconium.

The coating produced by this process may be regarded as an improved hot-dip aluminum coating in many respects, but as a protection against high temperature oxidation of ferrous materials it must be considered as something distinctly new.

The application of hot-dipped aluminum coatings is not a new idea. It has been attempted with a greater or lesser degree of success since aluminum has been available as a common metal. For the most part, methods for applying the aluminum were adopted from conventional tinning and galvanizing operations. Generally the suggested procedures failed to give an aluminum coating of sufficient quality to be of commercial interest.

However, special mention may be made of two processes which have recently achieved a

certain measure of commercial success. One of these is applicable only to steel sheet or strip, and involves passing material from a bright annealing furnace through a hydrogen-containing atmosphere into molten aluminum and out through a hydrogen-containing atmosphere. This produces a coating peppered with innumerable small pin holes, and having less than satisfactory adherence, and constitutes a process which is inflexible and requires high capital investment. The second procedure involves maintaining a very deep flux layer on top of the aluminum bath, holding the work in this layer long enough to raise its temperature almost to that of the aluminum, then lowering the work into the aluminum and allowing it to remain there long enough to coat it and finally withdrawing the work through the flux. The coating produced does not have optimum adherence, the aluminum bath is contaminated with large amounts of iron from the flux, and the procedure is very awkward and inconvenient for coating sizable pieces.

Hot-dipped aluminum or aluminum alloy coatings, particularly on iron or steel, are of great potential value for several reasons. The aluminum coating in itself is quite corrosion resistant in many cases, for example, being superior in this respect to a zinc coating. The aluminum is electropositive to iron in the presence of water in the same manner as zinc, affording galvanic protection. By virtue of its higher melting point and the greater inertness of its compounds with iron, an aluminum coating gives protection at much higher temperatures than do hot-dipped coatings of zinc, lead or tin.

In general there are two reasons why previously-known processes for hot-dip coating of iron or steel with aluminum or aluminum alloys have been unsuccessful or, at best, only partially successful. The first is the difficulty in securing complete coverage or wetting of the ferrous surface with the molten aluminum or aluminum alloy during the dipping operation.

BEST AVAILABLE COPY

This is due to the presence of oxide on the liquid aluminum surface under most all conditions, and to the difficulty of preparing a chemically clean surface on the ferrous material to be coated. There is some evidence that interfacial tension is quite high even with clean aluminum and ferrous surfaces. In effect, it is difficult to wet the ferrous surface with aluminum. Even when apparently complete coverage is obtained, as in the two commercial processes above noted, microscopic examination shows numerous small pin holes in the coating.

The second major difficulty in hot-dip aluminum coating is due to the rapid reaction of a large mass of liquid aluminum with iron, once wetting is obtained, with formation of an iron-aluminum intermetallic compound. This compound forms as a layer between the aluminum coat and the ferrous base material. Its physical properties are non-metallic in character, and it is friable and brittle. When a coated article is placed under stress, this compound layer cracks, primarily within its own thickness, and the overlying aluminum peels off. Usually this property of the coating is designated as low adherence.

It will be noted that steps which would normally be taken to overcome one of these major defects of previous processes for applying an aluminum coating will accentuate the other difficulty. For instance, wetting of a ferrous surface can be improved by longer immersion in, and higher temperature of, the aluminum dipping bath. But these factors favor greater reaction between the aluminum and iron, resulting in a thicker compound layer and low adhesion of the coating. On the other hand, reductions in time of immersion and in temperature minimize compound layer formation but lead to trouble in securing complete coverage of the ferrous surface. The present commercial processes are essentially attempts to compromise the conflicting requirements of these two problems. Consequently the resulting products are never completely satisfactory, and very frequently are of quite poor quality for the one reason or the other.

It is the primary object of this invention to eliminate the above described difficulties in the hot-dip coating of ferrous materials with aluminum or aluminum alloys, making it possible to produce this coating without compromising on quality in any respect. A further purpose is to produce a coating which affords outstanding protection to ferrous materials against oxidation at high temperatures. Still another object is to achieve these ends by a process which is both practical and economically feasible.

To the accomplishment of the above and related objects, this invention may be embodied in the steps described in the following description and illustrated in the accompanying drawings, attention being called to the fact, however, that the specific procedures described and illustrated are by way of illustration only and

that changes may be made therein, so long as the scope of the appended claims is not violated.

Fig. 1 is a diagrammatic flow sheet illustrating the steps in a preferred form of the process;

Fig. 2 is a similar flow sheet illustrating a slightly modified procedure;

Fig. 3 is a similar flow sheet showing an alternative procedure; and

Fig. 4 is an enlarged, fragmental sectional view of a piece of ferrous metal coated in accordance with the process of the present invention.

These purposes are accomplished by depositing a chromium coating 28 (Fig. 4) on the ferrous surface 29 and over this applying a hot-dip aluminum or aluminum alloy coating 30. The chromium coating is deposited galvanically from a fused metallic chloride solution of chromium chloride, or by electrodeposition if a thicker coating is desired. Wherever, in the present specification, reference is made to a chromium coating, it is to be understood that a coating of any one of the above-mentioned metals, having a solubility in liquid aluminum not exceeding 8% at 700°C., might be used instead.

It should be noted that the properties of fused chloride solutions are in many respects quite different from those of solutions of the same salts in aqueous and other oxygen-containing solvents. For example, the relative positions of the metals in the electromotive series changes with the solvent and, in such fused, non-aqueous solutions, may be at considerable variance from the commonly accepted version which is for aqueous solutions. In the fused chloride media described in this specification, chromium is definitely electronegative to iron and is readily displaced from solution by metallic iron.

Conventional galvanic chromium coatings are very readily wetted with aluminum, and thus aid in securing complete coverage or enshrouding of the ferrous material with aluminum. These coatings are completely free of pin holes. Heavy galvanic deposits and electrodeposits, however, are sometimes difficult to wet. In such instances the chromium coated article is coated with lead and the lead displaced with aluminum or aluminum alloy. In either case, the essential character of the resultant coating is the same, viz., an outer layer of aluminum or aluminum alloy and an intermediate layer of chromium.

The chromium is very effective as a "blocking" layer to prevent reaction of aluminum and iron to form the undesirable intermetallic compound. Microscopic examination of articles which have been provided with coatings in accordance with the present invention shows that the chromium layer is very distinct, the only evidence of alloying being that of chromium with the ferrous base material.

Consequently, the adhesion of the aluminum coating is excellent. The extent to which a ferrous sheet coated in this way can be formed or worked is limited only by the ductility of the aluminum coating and of the base metal itself.

As indicated above, the coating produced by this invention offers unusual protection to ferrous materials against oxidation at high temperatures. This can be attributed to the intermediate coating of chromium. Although the various reactions have not been exhaustively investigated, the following explanation covers the observed facts.

A distinction must be made between the reaction of aluminum and iron in the presence of excess aluminum, as in an aluminum dipping bath, and the reaction of aluminum and iron in the presence of a limited amount of aluminum, as in the case of a ferrous piece covered with an aluminum coating, when exposed to an elevated temperature. In the former case, and in the absence of a blocking layer, formation of the aluminum-iron compound layer proceeds rapidly. This compound, being of greater specific volume than the ferrous base material, develops cracks and fissures, both parallel to, and perpendicular to, the base metal surface. If immersion time is long enough, pieces of the compound break off and are floated away in the liquid aluminum. Apparently the compound is fairly impermeable to liquid aluminum and the reaction proceeds by aluminum penetrating to the ferrous surface through cracks in the compound layer. When pieces having coatings produced in this manner are exposed to elevated temperatures outside the aluminum bath, there is little further reaction, because of the relative impermeability of the compound and because of the fact that pieces of the compound cannot be floated away under these conditions. Consequently the aluminum metal on the surface burns away. By virtue of its friable nature, much of the compound layer flakes off. Eventually, the only protective coating left consists of a thin layer of iron-aluminum compound rich in iron.

When pieces provided with the coatings of the present invention are exposed to high temperatures, the chromium alloys with the ferrous base and, to a less extent, with the aluminum. The iron, penetrating through the chromium layer, then alloys very slowly with the aluminum. Some of the aluminum on the outside is oxidized and falls away. The final protective coating comprises a series of alloy layers, rich in aluminum on the outside and rich in iron on the inside. Other constituents of the original aluminum alloy and of the ferrous base material are similarly distributed. The chromium is found throughout the coating, as indicated by spectrographic examination and by X-ray diffraction studies. The existence of this series of alloy layers may

be observed by microscopic examination, or by careful dissolution of the coating with strong acids.

The details of a preferred form of the invention may be outlined as follows:

The material 20 (Fig. 1) to be coated, such as carbon steel for the following specific values, is first cleaned by conventional methods, as acid pickling, rinsing in hot water and drying. It is then introduced, without necessarily preheating the work, into the galvanic coating bath 21. This bath 21 consists of zinc chloride containing approximately 10% of the triple eutectic of sodium, potassium and lithium chlorides, approximately 5% ammonium chloride and a content of a chloride of the metal to be deposited, in this case chromium chloride, which is held between 0.2% and 3.0%, but preferably between 1.0% and 1.5%. The bath is held at a temperature of about 400° to 450°C.; and the optimum immersion time is 5 seconds plus the time necessary to remelt any salt which may be frozen on the work when it is introduced into the bath.

The work is removed from the galvanic coating bath and is cleaned of heavy metal salts by immersing the work in a fused alkali chloride bath 22 which is free of heavy metals. Preferably this bath consists of a mixture of sodium, potassium and lithium chlorides, with a layer 23 of alkali metal, alkaline earth metal or aluminum at the bottom of the container to remove heavy metals. The temperature of the chloride bath is held at about 650°C. An immersion time of 5 seconds is adequate to remove adhering salts from the preceding bath, but longer times are employed if necessary to heat the work.

The work is removed from the chloride wash bath, immersed in a molten aluminum or aluminum alloy bath 24 and held there, with gentle agitation, for 10 to 20 seconds. Except when a top flux 25 is used, as described below, the surface of this bath 24 is skimmed just before the work is introduced and just before it is removed. The temperature of the metal bath is held about 30°C. above the melting point of the aluminum or aluminum alloy. After removal of the work, excess aluminum is removed therefrom by any of the conventional methods.

The times of immersion and the temperatures of the first two baths are selected to bring the temperature of the work close to that of the aluminum bath. The overall time required for the whole operation is essentially that required to heat the work above the melting point of the aluminum or aluminum alloy.

There are several alternatives to various phases of the above process. The composition of the galvanic coating bath 21 may be varied over a wide range. The major portion of this bath, in effect the solvent, consists of a combination of one or more of the chlorides of zinc, sodium, potassium, lithium, calcium,

magnesium or barium. The identity and proportions of constituent chlorides is determined by requirements on melting point, fluidity, solubility for other bath components, and, to some extent, chemical reactivity. The zinc chloride content in the bath may be as high as 99%. In most cases a minimum of about 10% zinc chloride in the bath is desirable in order to hold an appreciable quantity of ammonium chloride in solution. The ammonium chloride content may be varied from about 1% to 10%, the optimum concentration depending on the degree of acidity and reducing potential required. The alkali metal chlorides and alkaline earth chlorides content may be varied between 0% and 99% and the chromium chloride content may be varied from about 0.2% to 3%. Other plating metals should be at a corresponding molar concentration. It should be noted that the temperature of the bath, its acidity and the plating metal concentration are interrelated, and a reduction in one of these factors requires a compensating increase in one or both of the others.

The plating metal can be added to the bath as a chloride or as any compound of the metal which will react with the bath to give a chloride of this metal. The fused salt baths above described are both strongly acidic and strongly reducing in character. Compounds which are readily converted to chlorides under these conditions include oxides, hydroxides, oxy-acids, salts of oxy-acids, carbonates, nitrates, salts of organic acids. It is desirable that these compounds be such that the products of their reaction with the bath, other than the plating metal chloride, either be constituents already present in the bath, as sodium or ammonium, or be volatile, as water, carbon dioxide, nitrogen oxides. Preferably these metal compounds are added to the bath in admixture with 1 to 3 times their weight of ammonium chloride, but this is essential only when the concentration of ammonium chloride in the bath is quite low. In some cases reaction is so rapid, as with sodium dichromate, that the metal compound must be added very slowly to avoid excessive foaming. In other cases, the reaction is quite slow, as with titanium dioxide, and some time must be allowed for the reaction to proceed before the bath can be used. The compounds actually used in practice for addition to the bath will be selected on the basis of such factors as cost and ease of handling.

The time of immersion in the galvanic plating bath will vary from values given above with different ferrous alloys and with different plating metals. Generally both longer times of immersion as well as high activity of the bath are required with the more refractory alloys.

Excessive time of immersion in the galvanic bath should be avoided in most cases. It results eventually in a roughened surface. Even when the attack upon the base metal is less severe,

the coating so obtained may be difficult to wet with aluminum and thus may require pre-coating with lead as suggested in flow sheet Fig. 3. The temperature of the galvanic bath may be varied from just above the melting point of the bath to about 650°C. The temperature selected in any particular instance will be determined by the chemical reactivity desired, which will be accelerated by elevated temperatures, and by the extent to which the work should be heated in this bath.

The chromium coating may be electrodeposited instead of being galvanically deposited. A much thicker chromium layer can be secured in this manner if it is desired. The bath is the same as that used for the galvanic coating. The procedure is the same, except that an electric current at suitable voltage is applied for the required time.

With electrodeposited coatings and with heavier galvanic coatings it is preferable to coat the work with lead before applying the aluminum or aluminum alloy coating. The work is taken directly from the chromium coating bath 21 of Fig. 3 to the lead bath and thence to the fused alkali chloride bath 22 and to the aluminum bath 24, wherein a layer of displaced lead will accumulate at the bottom.

The proportions of individual alkali chlorides in the wash bath 22 may be varied from the composition given in the preferred procedure described above. As a matter of economy, the lithium, chloride content may be reduced or eliminated. Alkaline earth chlorides, singly or in combination, may replace up to 50% of the alkali metal chlorides. A fixed requirement is that the melting point of the combination used be lower than the operating temperature of the succeeding bath.

The metal 23 carried in the alkali chloride bath described in the preferred procedure may be either sodium, calcium, magnesium or aluminum, or an alloy of these metals may be so used. The essentials are that the metal be electropositive to the heavy metal which it is desired to remove and that its specific gravity shall be such that it will remain at the bottom of the bath. When aluminum chloride is introduced, as by inclusion of aluminum metal, it is desirable to add a small proportion of alkali or alkaline earth fluoride, 5% to 10% to maintain high fluidity.

Ordinarily it is not desirable to hold the temperature of the fused alkali chloride wash bath 22 more than 50°C. below that of the following aluminum bath 24. It may be held at a higher temperature than the aluminum bath to speed up the operation. Time in this chloride bath is not critical, except as it affects the temperature of the work, and the work can be held here for extended periods without deleterious effects.

As an alternative procedure, the chloride wash bath 22 may be omitted, the work passing

directly from the chromium coating bath 21 to the aluminum bath 24 as suggested in flow sheet Fig. 2. The primary purpose of the wash bath is removal of heavy metal salts carried over on the work from the chromium coating bath. Zinc salts are especially objectionable in the aluminum bath since they form a complex zinc-aluminum oxide which makes the residual flux very viscous. The heavy metals also contaminate the aluminum, and consume appreciable quantities of aluminum metal. However, if the work is not too complex in design and if speed of operation is not important, this alternative can be employed.

Still another alternative is introduction of the work into the aluminum or aluminum alloy bath through a top flux 25, as suggested in Fig. 1. The composition of the top flux is the same as that described above for the chloride wash bath. Fluorides may be substituted for a small proportion, 5% to 10%, of the chlorides in some of the alternative compositions if higher fluidity is desired. An obvious requisite is that the melting point of the top flux be lower than that of the aluminum alloy being used. Such a top flux is highly desirable in continuous operations with sheet, strip or wire. It also eliminates the need for skimming before introduction of the work to the aluminum bath in discontinuous operations.

The work may be withdrawn through a top flux of substantially the above composition. This eliminates the need for skimming and reduces the incidence of flux spots in the coating, but tends to stain the surface of the coating. The work may also be drained of excess aluminum by withdrawing it through a deep top flux or holding it in a separate flux bath held at about the melting point of the aluminum or aluminum alloy.

This coating process is applicable with any alloy the major constituent of which is aluminum. In most instances a casting alloy is preferred, the aluminum-silicon alloys being superior to aluminum-magnesium alloys with respect both to coating operation and to the properties of the coating.

The temperature of the aluminum or aluminum alloy bath 24 is not particularly critical in the presence of the chromium blocking layer. It may be varied from about 25°C. above the melting point of the aluminum alloy to 200° or so above this point, the higher temperatures aiding in heating the work. The minimum immersion time permissible is that necessary to remove adhering salts from the work and to remelt any aluminum frozen on the work when the work is first introduced into the aluminum bath. The required immersion times for other blocking metals will vary from that for chromium, being longer in most cases. These times will also vary with the composition of the aluminum alloy being used. The work may be held in the aluminum bath for several minutes without injurious effects,

but excessively prolonged immersion should be avoided.

The following examples are given in order that this invention may be more fully understood:—

EXAMPLE No. 1

Pieces of 1010 carbon steel sheet were prepared for coating by degreasing, pickling in 5% muriatic acid, rinsing in hot water and drying. These were coated with chromium by dipping them into a bath of zinc chloride containing 10% of the triple eutectic of sodium, potassium and lithium chlorides, 5% ammonium chloride and 1% chromium chloride. The bath was held at 450°C. Dipping time was 8 seconds. The specimens were then placed in a bath consisting of 50% potassium chloride, 25% lithium chloride and 25% sodium chloride at 650°C. for 10 seconds. The pieces were then immersed for 20 seconds in a 95% aluminum—5% silicon bath at 670°C.

The aluminum-silicon coating obtained was smooth and continuous, with no detectable pin holes. Specimens could be bent back on themselves, 180°, with no flaking or peeling. Specimens were held in a rapid air stream at 1000°C. for 500 hours with no failure of the protective coating.

EXAMPLE No. 2

Specimens of 1010 carbon steel were coated with chromium in the same manner as in Example No. 1, except that the temperature of the bath was 500°C. They were then dipped directly into a 93% aluminum—7% silicon bath at 680°C. for 25 seconds. The coatings were excellent in regard to continuity and adhesion. Coated specimens were exposed to air at 1000°C. for 475 hours with no failure of the protective coating. Similar results were noted after 15 hours at 1100°C. and after 2 hours at 1250°C. Specimens of similar steel sheet coated with aluminum-silicon by one of the presently available commercial processes showed, under the same conditions, complete failure of the coating after 24 hours at 1000°C.

EXAMPLE No. 3

Pieces of type 310 stainless steel sheet were coated by the method described in Example No. 1. The aluminum-silicon coatings obtained were smooth, continuous and adherent. Specimens were heated in air at 1100°C. for 24 hours with no sign of failure.

EXAMPLE No. 4

Sections of a type 310 stainless steel casting were pickled, rinsed, dried and then coated with chromium by immersion for 25 seconds in a zinc chloride bath containing 5% sodium chloride, 5% potassium chloride, 7% ammonium chloride and 1% chromium chloride, held at a temperature of 600°C. The sections were then introduced directly into a 93% aluminum—7% silicon bath held at 690°C. After 30 seconds immersion, they were removed and shaken free of adhering molten metal. Complete coverage of the intricate

casting was obtained. Specimens held in air at 1100°C. for 75 hours showed no failure of the protective coating.

EXAMPLE No. 5

- 5 Specimens of cast iron were pickled in 5% muriatic acid, rinsed and dried. They were coated with chromium by immersion at 600°C. for 30 seconds in a zinc chloride bath containing 5% potassium chloride, 2% lithium chloride, 10 3% ammonium chloride and 1.5% chromium chloride. They were then introduced directly into a 93% aluminum—7% silicon bath at 690°C. Time of immersion was 25 seconds. They were removed and, before the coating 15 metal solidified, additional aluminum-silicon was cast around them. With these specimens, attempts to separate the aluminum-silicon from the cast iron resulted in breaks in the aluminum-silicon metal. Similar specimens, with 20 which the aluminum-silicon coating was applied according to a previous process when tested in this way exhibited separation of the aluminum-silicon alloy from the cast iron, the line of cleavage being along the aluminum- 25 iron compound layer.

EXAMPLE No. 6

- Pieces of 1010 carbon steel sheet were prepared for coating by degreasing, pickling in 5% hydrochloric acid, rinsing in hot water and drying. They were plated with nickel by 30 immersing for 6 seconds in a bath of zinc chloride containing 4% sodium chloride, 4% lithium chloride, 5% ammonium chloride and 0.5% nickel, added as the chloride. The bath 35 was held at 450°C. The steel specimens were taken directly from this bath into a 95% aluminum—5% silicon bath at 670°C. After 20 seconds immersion they were removed, excess aluminum-silicon removed by shaking, 40 and cooled.

- The aluminum-silicon coating was smooth and continuous, with no detectable pin-holes. Specimens were bent back on themselves, 180°, with no flaking or peeling. Other specimens were heated in air at 1100°C. for 24 45 hours with no indication of coating failure.

EXAMPLE No. 7

- Pieces of 1010 carbon steel were degreased, pickled in 5% hydrochloric acid, rinsed in hot 50 water and dried. They were plated with nickel by dipping for 15 seconds at 450°C. in a bath of zinc chloride containing 10% of the triple eutectic of sodium, potassium and lithium chlorides, 5% ammonium chloride and 0.5% 55 nickel, added as the chloride. They were coated with lead by passing through a zinc chloride flux containing 3% sodium chloride, 3% potassium chloride and 1% ammonium chloride into a lead bath at 550°C. for 5 60 seconds. Adhering flux was removed by dipping into a bath consisting of 60% potassium chloride, 25% lithium chloride and 15% sodium chloride at 650°C. for 5 seconds. The lead was displaced by agitating gently in a 65 95% aluminum—5% silicon bath at 680°C.

for 20 seconds.

The aluminum-silicon coating was smooth and continuous. Adherence of the coating was excellent, as shown by absence of flaking and peeling with severe bending and distortion. 70 Upon exposure in air at 1275°C. for 3 hours, the coating was smooth, bright and showed no evidence of failure.

EXAMPLE No. 8

Pieces of type 410 stainless steel were plated 75 with nickel and coated with aluminum-silicon by the procedure described under Example No. 6. The resultant coating was smooth, continuous, of excellent adherence and withstood exposure in air at 1100°C. for 28 hours 80 without any sign of failure.

EXAMPLE No. 9

Pieces of type 410 stainless steel were plated with nickel and coated with aluminum-silicon by the procedure described under Example 85 No. 7. The coating obtained was smooth, continuous and showed excellent adherence under severe distortion.

EXAMPLE No. 10

Pieces of type 310 stainless steel sheet were 90 plated with nickel and coated with aluminum-silicon by the procedure described under Example No. 7. The coating obtained was smooth, continuous, of excellent adherence and was sound after exposure in air at 1100°C. 95 for 3 hours.

EXAMPLE No. 11

Pieces of type 410 stainless steel sheet were degreased, pickled in 5% muriatic acid, rinsed in hot water and dried. They were plated with 100 molybdenum by immersing for 20 seconds at 500°C. in a bath of zinc chloride containing 10% of the triple eutectic of sodium, potassium and lithium chlorides, 5% ammonium chloride and 0.5% molybdenum, added as ammonium 105 molybdate. They were coated with lead by dipping through a zinc chloride flux containing 3% potassium chloride, 3% lithium chloride and 3% ammonium chloride into a lead bath at 550°C. for 10 seconds. The adhering flux 110 was removed by dipping into a bath consisting of 60% potassium chloride, 25% lithium chloride and 15% sodium chloride at 650°C. for 5 seconds. The lead was displaced by 115 agitating gently in a 95% aluminum—5% silicon bath at 700°C. for 20 seconds.

These coatings were excellent in regard to appearance, continuity and adherence. After exposure in air at 1100°C. for 24 hours the residual coatings were bright, smooth and 120 affording complete protection to the base steel.

EXAMPLE No. 12

Pieces of 1010 carbon steel sheet were plated 125 with molybdenum and coated with aluminum-silicon by the procedure described under Example No. 11. The coatings were of excellent continuity and adherence, and were giving complete protection to the steel after exposure in air at 1100°C. for 3 hours. 130

EXAMPLE No. 13

Pieces of 1010 carbon steel sheet were degreased, pickled in 5% muriatic acid, rinsed in hot water and dried. They were plated with titanium by dipping for 20 seconds at 500°C. into a bath consisting of the triple eutectic of potassium, sodium and lithium chlorides, saturated with ammonium chloride and containing 0.5% titanium, added as titanium dioxide with the ammonium chloride. They were coated with lead by passing through a zinc chloride flux containing 3% potassium chloride, 3% lithium chloride and 3% ammonium chloride into a lead bath at 550°C. for 20 seconds. The lead was displaced by agitating gently in a 95% aluminum-5% silicon bath at 700°C. for 20 seconds.

The coatings were continuous, with no detectable pin-holes. They exhibited excellent adherence. They were still sound after exposure in air at 1000°C. for 8 hours.

EXAMPLE No. 14

Pieces of 1010 carbon steel sheet were degreased, pickled in 5% muriatic acid, rinsed in hot water and dried. They were plated with lead by dipping for 10 seconds at 450°C. into a zinc chloride bath containing 5% sodium chloride, 3% lithium chloride, 5% ammonium chloride and 0.5% lead, added as the chloride. They were coated with aluminum-silicon by immersing in a 97% aluminum-3% silicon bath at 700°C. for 20 seconds. These coatings were excellent with respect to appearance, continuity and adherence.

EXAMPLE No. 15

Pieces of 1010 carbon steel sheet of various thicknesses were plated with cobalt by immersing them for 20 seconds at 450°C. in a zinc chloride bath containing 10% of the triple eutectic of sodium, potassium and lithium chlorides, 5% ammonium chloride and 0.3% cobalt, introduced as the nitrate. Adhering heavy metal salts were removed by dipping for 2 seconds at 550°C. in a bath consisting of the triple eutectic of sodium, potassium and lithium chlorides plus 5% sodium fluoride. They were then coated with 97% aluminum-3% silicon by immersing them with gentle agitation in the aluminum-silicon bath at 690°C. for 20 seconds.

Bright, smooth and continuous coatings were obtained. Adhesion of aluminum-silicon was good. The coatings were sound and affording complete protection to the steel after exposure in air at 1000°C. for 15 hours.

EXAMPLE No. 16

Pieces of 1010 carbon steel sheet of various thicknesses were plated with manganese by holding for 12 seconds at 450°C. in a bath consisting of zinc chloride with 10% of the triple eutectic of sodium, potassium and lithium chlorides, 5% ammonium chloride and 0.5% manganese, added as potassium permanganate. Heavy metal salts were removed by washing for 2 seconds at 550°C. in

the sodium, potassium and lithium chloride eutectic containing 5% sodium fluoride. The plated pieces were immersed for 10 seconds in a 97% aluminum-3% silicon bath at 680°C.

The aluminum-silicon coatings obtained were bright, smooth and continuous. Adherence of the coating was good. After exposure in air at 1000°C. for 15 hours the coatings were sound and affording complete protection to the steel.

EXAMPLE No. 17

Specimens of 1010 carbon steel sheet of various gauges were plated with zirconium by immersing for 10 to 15 seconds in a zinc chloride bath containing 10% of the sodium, potassium and lithium chloride eutectic, 5% ammonium chloride and 0.3% zirconium, added as zirconyl nitrate. The adhering heavy metal salts were washed off in a bath of the sodium, potassium and lithium triple eutectic by dipping the pieces for 3 seconds at 600°C. The zirconium plated pieces were dipped in 97% aluminum-3% silicon at 680°C. for 10 seconds.

Continuous, bright and very smooth aluminum-silicon coatings were obtained. Adhesion was excellent. Coated pieces exposed in air at 1000°C. for 15 hours were completely sound.

EXAMPLE No. 18

Pieces of 1010 carbon steel sheet of various thicknesses were plated with tungsten by immersing for 15 seconds at 450°C. in a bath consisting of zinc chloride containing 10% of sodium, potassium and lithium chlorides, 5% ammonium chloride and 0.5% tungsten, added as sodium tungstate. Adhering heavy metal salts were removed by dipping for 5 seconds in the alkali chloride triple eutectic at 550°C. The pieces were then immersed in 97% aluminum-3% silicon at 700°C. for 20 seconds.

The aluminum-silicon coatings were bright, smooth and continuous. Adhesion was good. Coatings were sound after exposure in air at 1000°C. for 15 hours.

This coating process is applicable to any ferrous article, including not only those which are predominantly ferrous but the alloys in which iron is present only in a small but significant amount. The range in composition of these ferrous materials is indicated in the following examples:—

EXAMPLE No. 19

Specimens of Multimet (Registered Trade Mark) (AMS 5532) sheet 0.050 in. thick were plated with chromium by immersing for 55 seconds in a zinc chloride bath containing 10% of the sodium, potassium and lithium chloride eutectic, 8% ammonium chloride and 0.5% chromium added as potassium dichromate. Temperature of the bath was held at 500°C. Adhering heavy metal salts were washed off in a bath of the sodium, potassium and lithium triple eutectic by dipping for 3 seconds at 550°C. The pieces were then immersed in

87% aluminum-13% silicon at 610°C. for 70 seconds, removed and shaken free of excess molten metal.

The coatings were bright, smooth and continuous. Adhesion was very good. The coatings were sound after exposure in air at 1100°C. for 12 hours. The nominal composition of Multimet is: 21% chromium, 20% nickel, 20% cobalt, 3% molybdenum, 3% tungsten, 1% niobium and 32% iron.

EXAMPLE No. 20

Pieces of Inconel (Registered Trade Mark) (AMS 5540) sheet 0.050 in. thick were plated with zirconium by immersing for 120 seconds in a zinc chloride bath containing 10% of the sodium, potassium and lithium chloride eutectic, 6% ammonium chloride and 0.4% zirconium added as zirconyl nitrate. Temperature of the bath was held at 500°C. The adhering heavy metal salts were removed by dipping for 3 seconds in the alkali chloride triple eutectic at 550°C. The specimens were immersed for 90 seconds in 87% aluminum-13% silicon at 610°C., removed and shaken free of excess molten metal.

The aluminum-silicon coatings were bright, smooth and continuous. Adhesion was good. The coatings were sound after exposure in air at 1100°C. for 12 hours. The nominal composition if Inconel is: 78% nickel, 15% chromium and 7% iron.

WHAT WE CLAIM IS:—

1. A process for coating ferrous metal including the steps of cleaning the surface of the work to be coated, then plating the work in a fused chloride bath which consists of ammonium chloride and at least one chloride selected from the group consisting of the chlorides of zinc, sodium, potassium, lithium, calcium, magnesium and barium at a temperature between the melting point of the bath and about 650°C., with a non-ferrous metal having a solubility in liquid aluminum not exceeding 8% by weight at 700°C., said bath being substantially water-free and oxygen-free and including the chloride of the metal to be deposited on the work in an amount between 0.2% and 3.0% of the mass of the bath, and then dipping the work in a molten metal bath whose major constituent is aluminum.

2. A process as set forth in claim 1, including prior to the dipping of the work in said molten metal, the step of cleaning heavy metal salts from the work by immersing the work in a bath consisting of fused alkali chlorides and/or alkaline earth chlorides and which is free of heavy metals.

3. The process as set forth in claim 1, in which the fused chloride bath consists of zinc chloride, the triple eutectic of sodium chloride, potassium chloride and lithium chloride, and ammonium chloride, together with the chloride of said metal to be deposited.

4. The process as set forth in claim 3, in which the chloride bath contains approxi-

mately 10% of the said eutectic and approximately 5% of ammonium chloride.

5. The process as set forth in claims 2 and 3, in which the fused alkali chloride bath consists of a mixture of sodium chloride, potassium chloride and lithium chloride.

6. The process as set forth in claim 5, in which a layer of metal, selected from the group consisting of sodium, calcium, magnesium and aluminum, is maintained at the bottom of the fused alkali chloride bath.

7. The process as set forth in claim 1, in which the fused chloride bath consists of zinc chloride 0% to 99%, alkali chlorides and alkaline earth chlorides 0% to 99%, ammonium chloride 1% to 10%, and the chloride of the metal to be deposited, 0.2% to 3% by weight.

8. The process as set forth in claim 7, in which the alkali chlorides are sodium chloride, potassium chloride and lithium chloride.

9. The process as set forth in claim 7, in which the alkali chlorides are sodium chloride and potassium chloride.

10. The process as set forth in claim 1, in which the fused chloride bath consists of zinc chloride 0% to 99%, alkaline earth chlorides 0% to 99%, ammonium chloride 1% to 10%, and the chloride of the metal to be deposited, 0.2% to 3% by weight.

11. The process as set forth in claim 1, in which the plating step is accomplished through electro-deposition by applying an electric current through the bath.

12. The process as set forth in claim 1, including the step of introducing the work to the molten bath whose major constituent is aluminum through a top flux consisting of a mixture of sodium chloride, potassium chloride and lithium chloride.

13. A process as set forth in claim 1, including, subsequent to said fused chloride bath, the step of dipping the work in a molten lead bath, to coat the work with lead, and then, while the lead coat continues to adhere to the work, dipping the work in a molten metal bath whose major constituent is aluminum to displace the lead coating with a coating of the metal of said last-named bath.

14. A process as set forth in claim 2, in which said cleaning bath consists of a fused mixture of sodium chloride, potassium chloride and lithium chloride together with an alkali fluoride, in the proportion of 5% to 10% of the mass of the bath, to maintain high fluidity of the bath, said bath being free of heavy metals.

15. A process as set forth in claim 14, in which a layer of aluminum is carried at the bottom of the bath.

16. A process as set forth in claim 1, in which said dipping the work in a molten metal bath whose major constituent is aluminum is effected by introducing the work to the last-named bath through a top flux consisting of a mixture of sodium chloride, potassium chloride

and lithium chloride and 5% to 10% of alkali fluorides.

17. A process for coating ferrous metal substantially as herein described and shown
5 in the accompanying drawings.

For the Applicants:

FRANK B. DEHN & CO.

Chartered Patent Agents,
Kingsway House, 103, Kingsway,
London, W.C.2.

Printed for Her Majesty's Stationery Office by J. Looker Ltd., Poole, Dorset. 1962.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies
may be obtained.

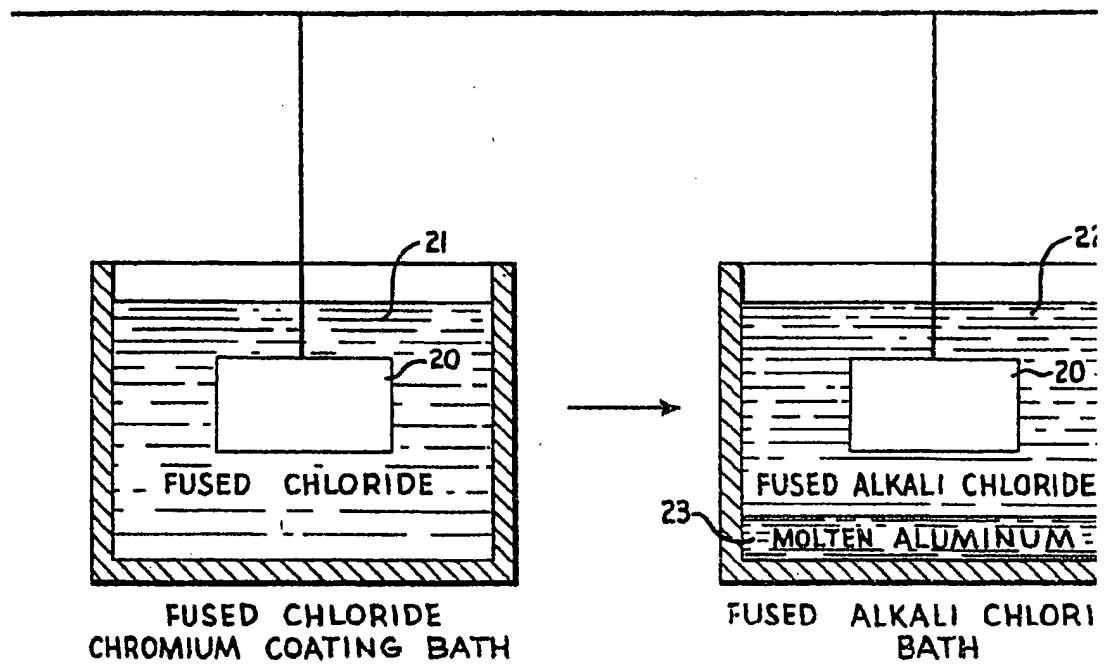


FIG. 1

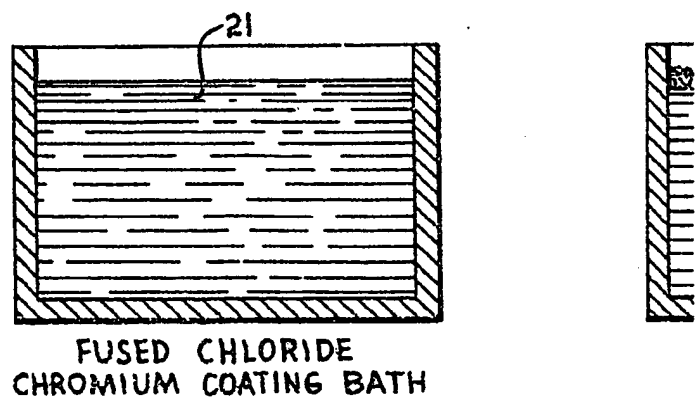


FIG. 2

896,866 COMPLETE SPECIFICATION

2 SHEETS

This drawing is a reproduction of
the Original on a reduced scale.

SHEET 1

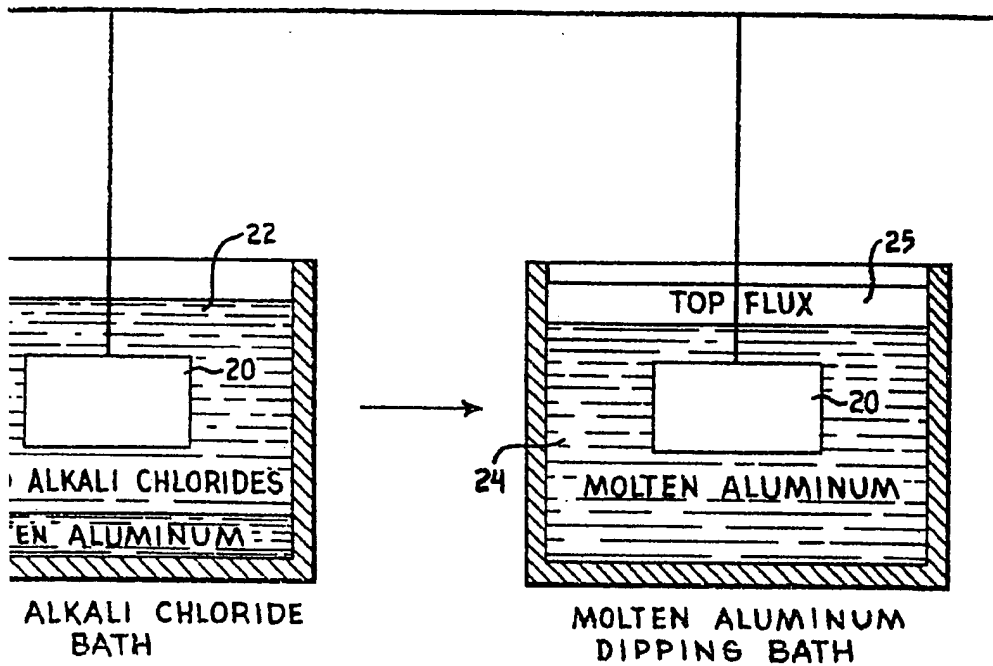


FIG. 1

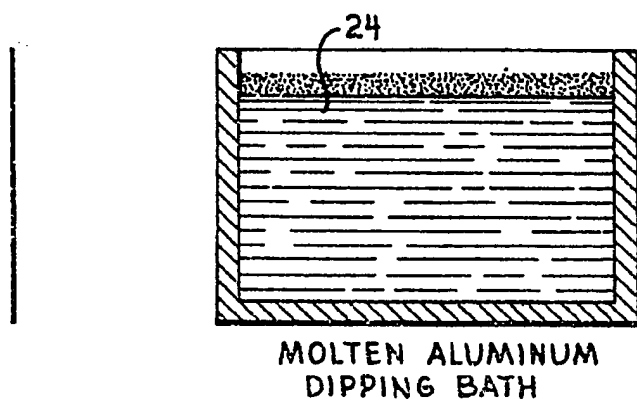
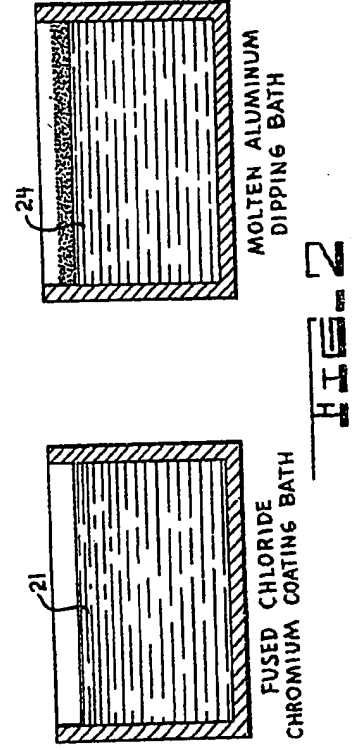
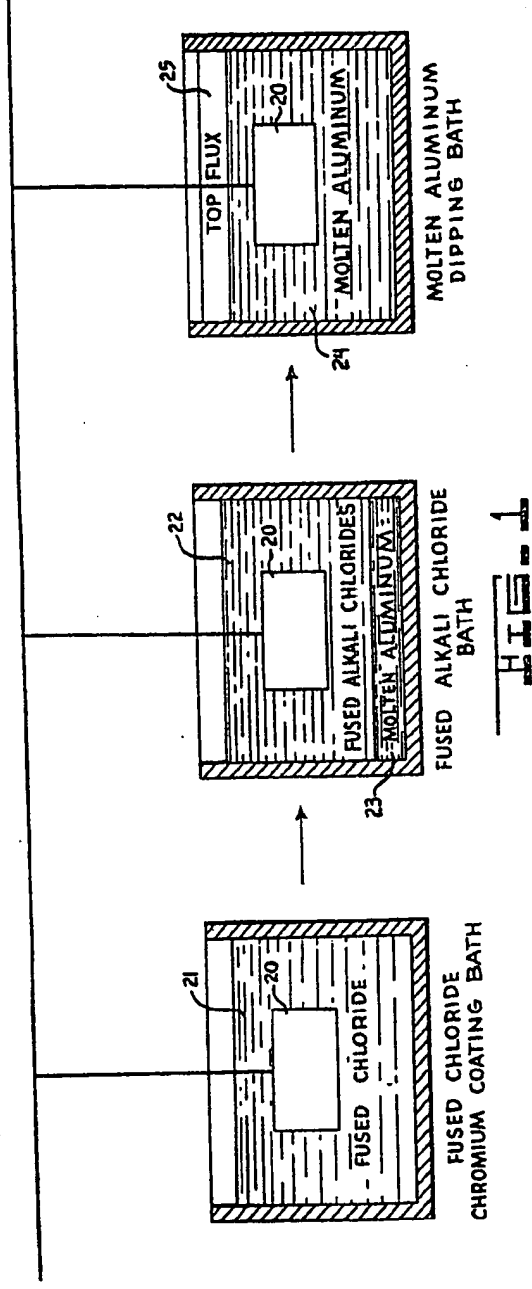
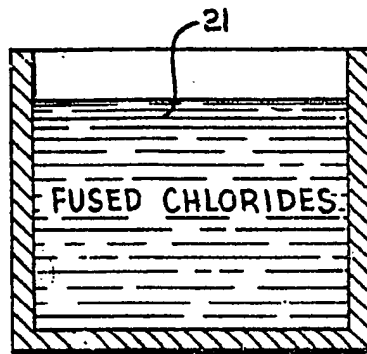
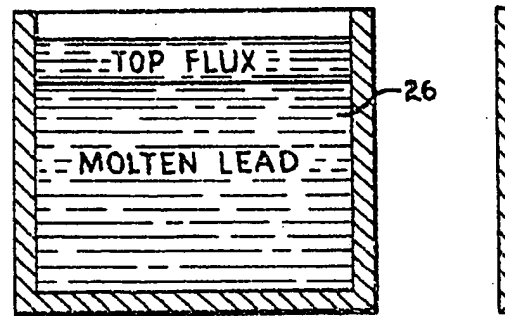


FIG. 2





FUSED CHLORIDE
CHROMIUM COATING BATH



MOLTEN LEAD
DIPPING BATH

FIG.

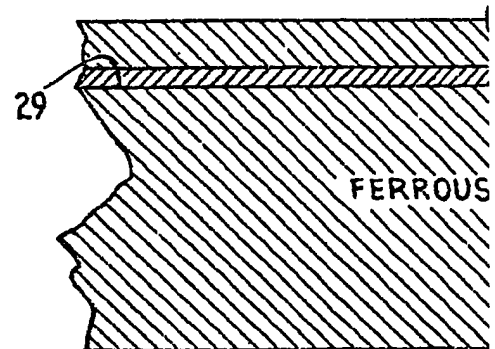


FIG.

896,866

COMPLETE SPECIFICATION

2 SHEETS

This drawing is a reproduction of
the Original on a reduced scale.

SHEET 2

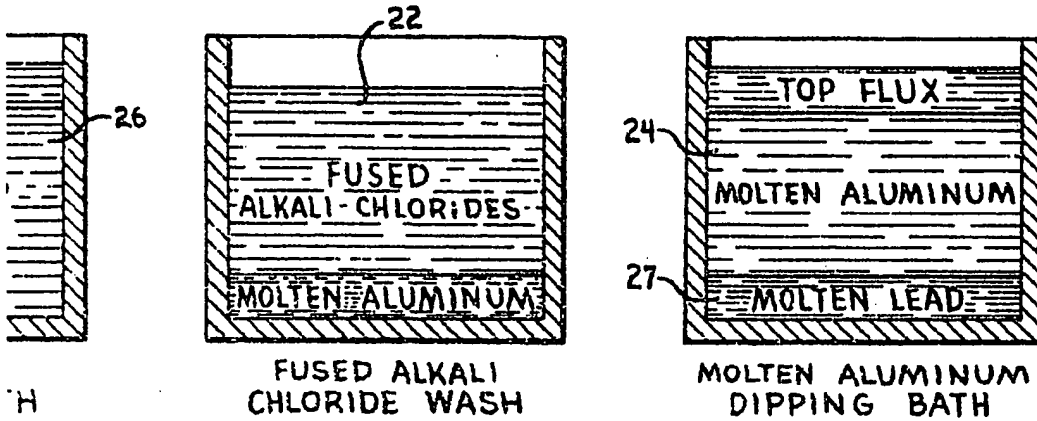


FIG. 3

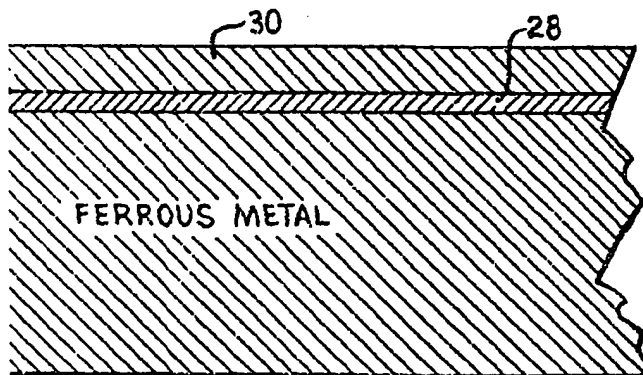


FIG. 4

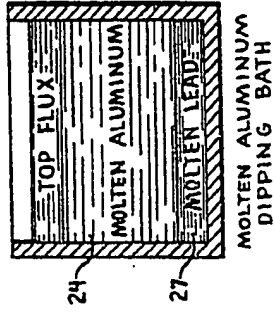
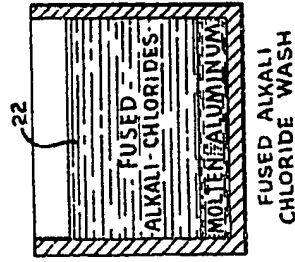
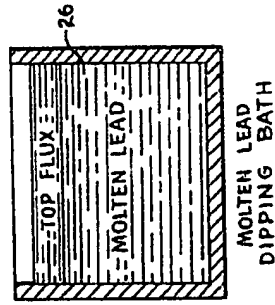
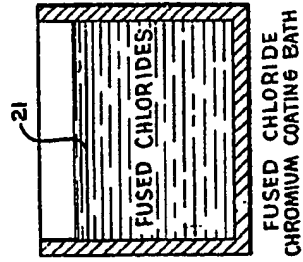


FIG. 3

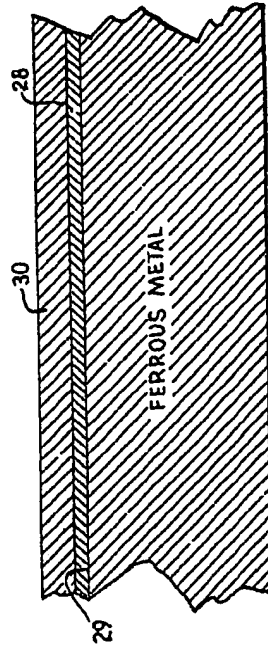


FIG. 4

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☒ **FADED TEXT OR DRAWING**
- ☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.